

4. CONCEPTUAL DESIGN AND MASS BALANCE FRAMEWORK FOR TRIM.FaTE

This chapter, building on the definitions and spatial and temporal concepts discussed in Chapter 3, presents the overall logic implemented in TRIM.FaTE for expressing transport and transformation of chemicals in a multimedia environment. Specifically, this chapter discusses and illustrates the mass balance approach and describes the processes simulated in TRIM.FaTE. The actual algorithms used to implement the approach are documented in Volume II.

4.1 CONCEPTUAL DESIGN

TRIM.FaTE calculates, given an initial mass inventory and mass inputs over time from one or more sources, the mass of one or more chemicals being modeled in each compartment in the modeled system for each simulation time step. With the volume and estimated chemical mass of each compartment, TRIM.FaTE can then calculate the concentration of each chemical in each compartment at each time step.

The development of TRIM.FaTE began with a conceptual diagram of the relationships and processes that affect chemical transport within the environment. The current version of this diagram is shown in Figure 4-1. In this figure, biotic compartments are represented by rectangles and abiotic compartments are represented by ovals. The various lines illustrate the potential chemical transfers between each of the components of the ecosystem.

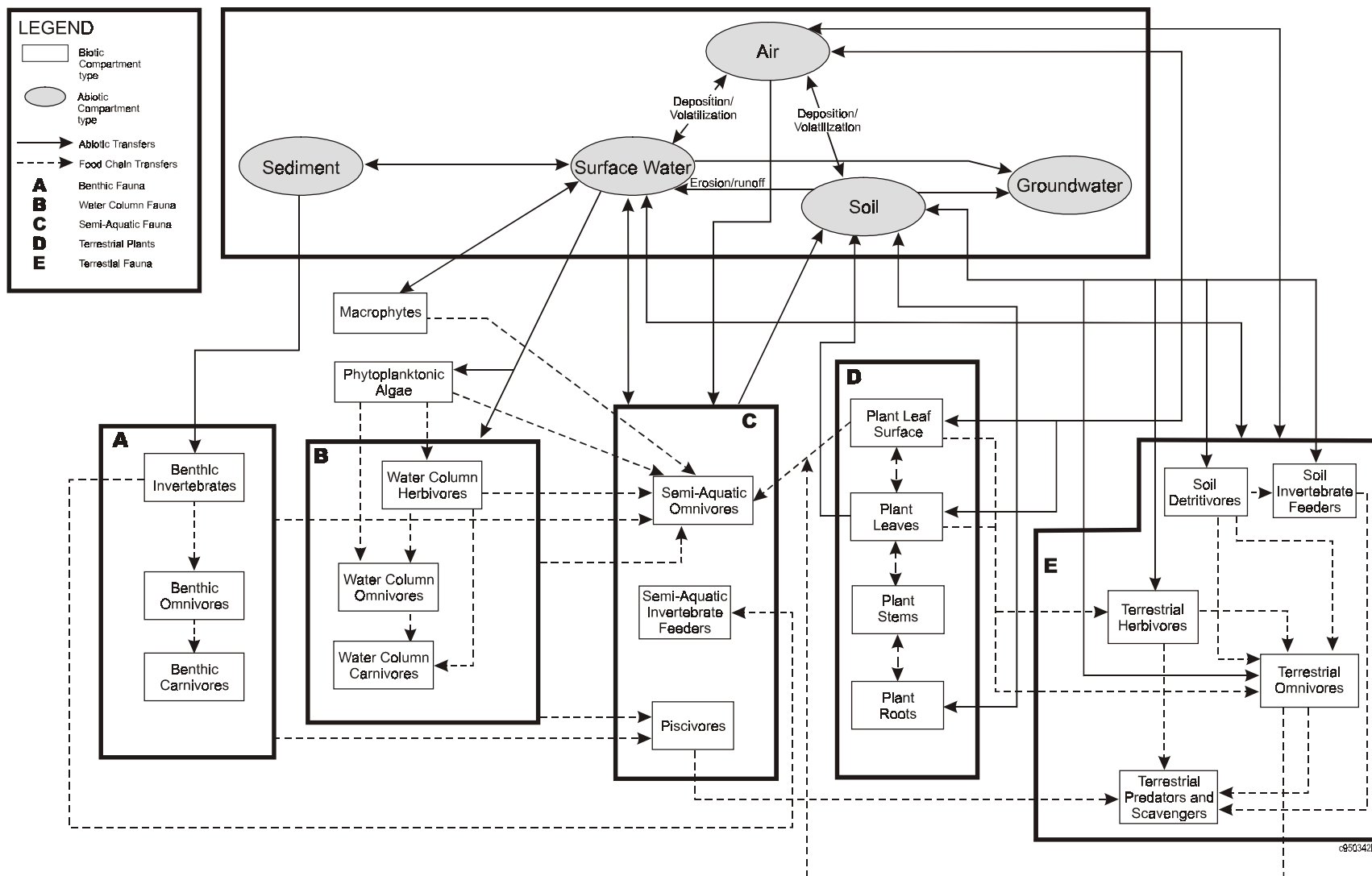
4.2 GOVERNING MASS BALANCE EQUATIONS

TRIM.FaTE has been developed with an emphasis on conserving chemical mass. This means that the entire quantity of a chemical input to the system is tracked throughout the system being modeled. When applied to a specific compartment (*e.g.*, soil, or a mouse population), this implies that, over a given time period, the amount of the chemical in the compartment at the end of the period is equal to the amount of the chemical in the compartment at the beginning of the period, plus the gains of the chemical that occurred during the time period, minus the chemical that was lost from the compartment during the time period.

To date, the mass balance approach has been implemented primarily for first-order linear processes. Therefore, this discussion is limited to algorithms of this type. It is important to note that higher order non-linear methods can also be implemented within this structure.

First-order transfers between compartments are described by transfer factors, referred to as T-factors. In most cases, T-factors are in units of inverse time. Technically, the units of a T-factor depend on the sending and receiving chemicals, as what is actually being preserved across the exchange is the amount of “core” chemical present in all transforming chemicals. The T-factor is the instantaneous flux of this “core” compound per amount of the compound in the sending compartment. The definition of the “core” compound depends on the particular chemicals being considered (*e.g.*, for the test case the core compound is an Hg atom).

Figure 4-1
Conceptual Diagram for TRIM.FaTE^a



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^a Chemical transformation processes are not depicted but may occur in all compartment types. Transformation products may be tracked in TRIM.FaTE or transferred out of compartments to sinks.

In most cases, it is expected that the molecular weights of the inter-transforming chemicals will be similar, and so preservation of the “core” compound will be essentially equivalent to preservation of mass. Significant differences between the preservation of “core” compound and the preservation of mass occur only if the sending and receiving chemicals have very different molecular weights. This has not been the case to date, but may occur as the model is applied to other transforming chemicals.

The preservation of “core” compound and the preservation of mass would be identical if the time-dependent masses of the reaction products were estimated simultaneously for each chemical of interest. Given the current computation and logistical demands of modeling transformation in many compartments, this is not seen as a practical general solution.

A simplification of a first-order transfer process is shown in the top part of Figure 4-2 for a system of one chemical, two compartments, and two transformation sinks, where transformation is treated as an irreversible loss. Denoting by $N_a(t)$ and $N_b(t)$ the mass of chemical in compartments a and b , respectively (in units of *mass*), it can be seen that:

$$\text{Chemical gains for compartment } a = S_a + T_{ba}N_b \quad (1)$$

$$\text{Chemical losses for compartment } a = T_{ab}N_a + R_aN_a \quad (2)$$

and

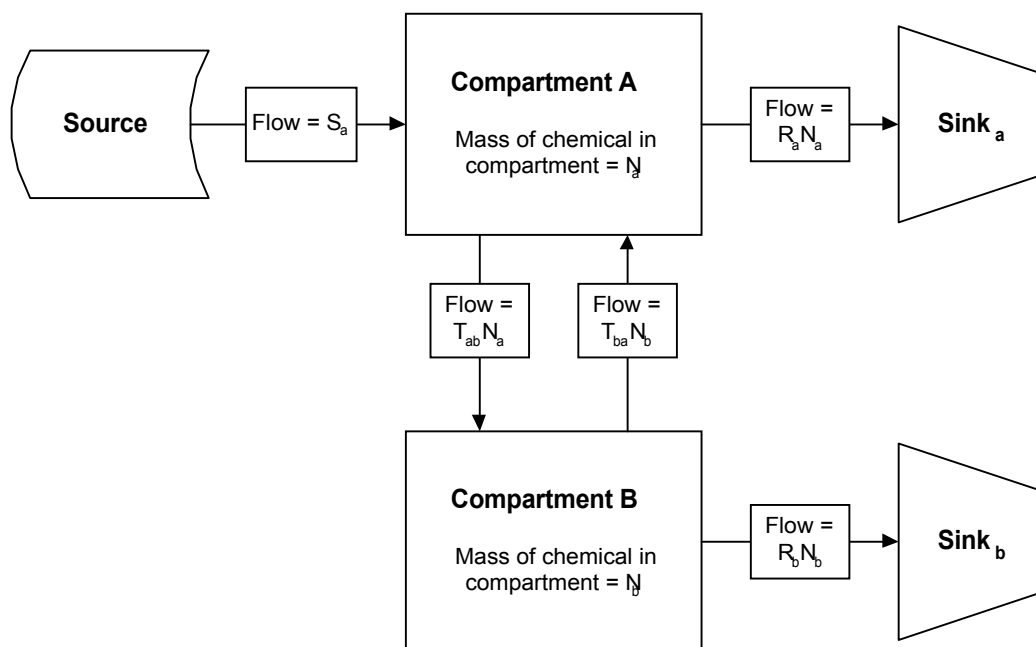
$$\text{Chemical gains for compartment } b = T_{ab}N_a \quad (3)$$

$$\text{Chemical losses for compartment } b = T_{ba}N_b + R_bN_b \quad (4)$$

where:

N_a	=	mass of chemical in compartment a, units of <i>mass</i>
N_b	=	mass of chemical in compartment b, units of <i>mass</i>
S_a	=	chemical source outputting to compartment a , units of <i>mass/time</i>
T_{ab}	=	transfer factor for movement of chemical from compartment a to compartment b during simulation time step, units of <i>/time</i>
T_{ba}	=	transfer factor for movement of chemical from compartment b to compartment a during simulation time step, units of <i>/time</i>
R_a	=	reaction loss of chemical in compartment a , units of <i>/time</i>
R_b	=	reaction loss of chemical in compartment b , units of <i>/time</i> .

Figure 4-2
Example of First-order Transfer Processes for Two Compartments, One Chemical
(Transformation Treated as Irreversible Sink)



$$\begin{bmatrix} dN_a/dt \\ dN_b/dt \\ dSink_a/dt \\ dSink_b/dt \end{bmatrix} = \begin{bmatrix} -(T_{ab}+R_a) & T_{ba} & 0 & 0 \\ T_{ab} & -(T_{ba}+R_b) & 0 & 0 \\ R_a & 0 & 0 & 0 \\ 0 & R_b & 0 & 0 \end{bmatrix} \begin{bmatrix} N_a \\ N_b \\ Sink_a \\ Sink_b \end{bmatrix} + \begin{bmatrix} S_a \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (5)$$

The constraint that mass balance must be preserved means that, over any time interval, the change in mass in a compartment is equal to the gains minus the losses in mass over the time interval. The instantaneous change in mass with respect to time is the derivative with respect to time, denoted by dN/dt . Thus, the mass balance constraint, when applied to the simple system discussed here, yields a system of two linked differential equations:

$$\frac{dN_a}{dt} = S_a + T_{ba}N_b - (R_a + T_{ab})N_a \quad (6)$$

$$\frac{dN_b}{dt} = T_{ab}N_a - (R_b + T_{ba})N_b \quad (7)$$

Additional terms are needed to properly account for the chemical mass. In particular, the fate of the chemicals after reacting must be tracked. For this reason, two additional compartments are added to the system, and serve as the repository of the chemicals after reaction. These are referred to as “sinks,” since after the chemical is transferred into these compartments, it no longer moves to any other compartments. While the chemical would continue to move in its altered form throughout the system, this movement is not of interest in this example. Denoting by $Sink_a$ and $Sink_b$, the mass in the reaction sinks for compartments a and b , respectively, the complete system is:

$$\frac{dN_a}{dt} = S_a + T_{ba}N_b - (R_a + T_{ab})N_a \quad (8)$$

$$\frac{dN_b}{dt} = T_{ab}N_a - (R_b + T_{ba})N_b \quad (9)$$

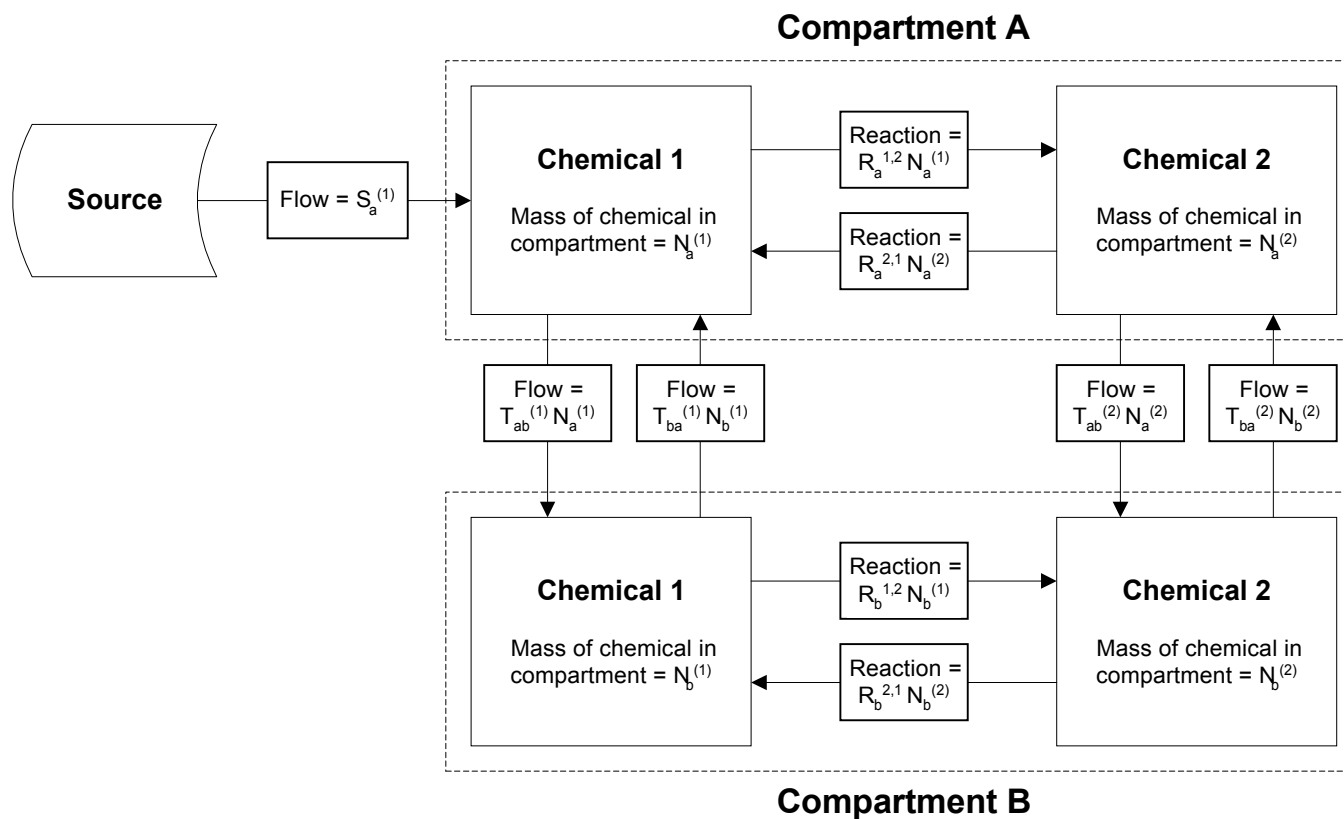
$$\frac{dSink_a}{dt} = R_aN_a \quad (10)$$

$$\frac{dSink_b}{dt} = R_bN_b \quad (11)$$

This system of equations is shown in matrix form in Equation (5) at the bottom of Figure 4-2.

If the fate of the transformed chemical is of interest, and the necessary algorithms and input data are available for the transformed chemical, then the mass balance approach can be modified accordingly. Figure 4-3 shows a generalization of the previous example, including the matrix form of the system [Equation (12)], to the case where the transformed chemical is modeled in addition to the chemical being transferred. In this case, transfer factors are added for the transformed chemical to account for additional possible transfers.

Figure 4-3
Example of First-order Transfer Processes for Two Compartments, Two Chemicals
(Chemicals 1 and 2 in Reversible Transformation Process; Transformation Products Tracked)



$$\begin{bmatrix} dN_a^{(1)}/dt \\ dN_b^{(1)}/dt \\ dN_a^{(2)}/dt \\ dN_b^{(2)}/dt \end{bmatrix} = \begin{bmatrix} -(T_{ab}^{(1)} + R_a^{1,2}) & T_{ba}^{(1)} & R_a^{2,1} & 0 \\ T_{ab}^{(1)} & -(T_{ba}^{(1)} + R_b^{1,2}) & 0 & R_b^{2,1} \\ R_a^{1,2} & 0 & -(T_{ab}^{(2)} + R_a^{2,1}) & T_{ba}^{(2)} \\ 0 & R_b^{1,2} & T_{ab}^{(2)} & -(T_{ba}^{(2)} + R_b^{2,1}) \end{bmatrix} \begin{bmatrix} N_a^{(1)} \\ N_b^{(1)} \\ N_a^{(2)} \\ N_b^{(2)} \end{bmatrix} + \begin{bmatrix} S_a^{(1)} \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (12)$$

Applying this same approach to a general system with M compartments (including all sinks), and allowing the transfer factors and source terms to depend on time as well, results in a system of linked differential equations of the form:

$$\frac{d}{dt}\vec{N} = A(t)\vec{N}(t) + \vec{s}(t), \quad \vec{N}(t_0) = \vec{N}_0 \quad (13)$$

where:

- $\vec{N}(t)$ = an M -dimensional vector whose i th entry is the mass in the i th compartment
- $A(t)$ = an $M \times M$ time-dependent matrix
- $\vec{s}(t)$ = an M -dimensional vector accounting for the source terms in each compartment.

The matrix $A(t)$ is referred to as the *transition matrix* for the system. This term is borrowed from Markov theory (Schneider and Barker 1989), although the model is not strictly a Markov process. The vector $\vec{s}(t)$ accounts for pollutant sources located within specific compartments. The vector \vec{N}_0 is the initial distribution of mass among the compartments.

4.3 PHASES

There are multiple environmental phases within many of the compartments in TRIM.FaTE. The most common phases are liquid, gas, and solid, which are assumed to be at chemical equilibrium within a compartment in this model unless otherwise specified. Other phases may include biotic phases (*e.g.*, algae in surface water). The adjacent text box lists the phases currently implemented in TRIM.FaTE for each medium.

In any compartment, the total amount of chemical present is made up of the sum of the amounts in the different phases. Because chemical equilibrium among phases is assumed, the ratios of the concentrations in the individual phases are constant for a given chemical. The fraction of the chemical that is in each phase in a compartment can easily be calculated. The chemical mass in each phase is tracked in TRIM.FaTE because transfer factors are sometimes phase dependent (*i.e.*, the transfer factor for particle deposition from air is dependent on chemical mass in the particle

**PHASES CURRENTLY
IMPLEMENTED IN TRIM.FaTE (listed
by medium)**

Air

- vapor
- suspended particulate

Soil

- soil pore water
- vapor
- soil solids

Surface water

- suspended solids
- water
- algae

Sediment

- sediment pore water
- sediment solids

phase of air). The mathematical details related to implementation of phases in TRIM.FaTE are presented in Chapter 2 of Volume II of the TRIM.FaTE TSD (U.S. EPA 1999d).

4.4 FATE, TRANSFORMATION, AND TRANSPORT PROCESSES

In TRIM.FaTE, the following processes are addressed and implemented as first-order processes for the modeling of the transfer and transformation of chemicals.

- Advective processes;
- Diffusive processes;
- Dispersive processes;
- Biotic processes; and
- Reaction and transformation.

More detailed explanation of the mathematical representation of these processes and documentation of all of the currently implemented algorithms are presented in Volume II of the TRIM.FaTE TSD (U.S. EPA 1999d).

4.4.1 ADVECTIVE PROCESSES

An advective process is one in which a chemical is transported within a given medium that is moving from one compartment to another. Mackay (1991) refers to this as a “piggyback” process, in which a chemical is “piggybacking” on material that is moving from one place to another for reasons unrelated to the presence of the chemical. Advective processes are modeled using first-order methods in TRIM.FaTE. Mathematically, all that is required to calculate the advective flux is the velocity of the moving phase and the amount of the chemical that is in the moving phase. Examples of advective processes considered for transport of a chemical are: erosion from a surface soil compartment to a surface water compartment, runoff from a surface soil compartment to a surface water compartment, and advective transport from one air compartment to another due to the wind field.

4.4.2 DIFFUSIVE PROCESSES

In a diffusive process, a chemical is transported from one compartment to another as a result of the magnitude and direction of the concentration differences between the two compartments at the interface between the two locations. Examples of diffusive processes considered include exchange between air compartments and soil or surface water compartments, exchange between benthic sediment compartments and surface water compartments, and exchange between air compartments. Models for diffusion frequently use non-first-order methods; however, these are often approximated with first-order methods. All diffusive processes are currently modeled in TRIM.FaTE using first-order methods. Diffusion rates are based on the compartment concentrations at the beginning of each simulation time step.

4.4.3 DISPERSION

Dispersion refers to the “spreading out” of a chemical during advective transport, and may result in movement perpendicular to the direction of advective flow. In TRIM.FaTE, dispersion is explicitly addressed (as a first-order process) in transfers between surface water compartment types. For surface water dispersion, the methods in the Water Quality Analysis Simulation Program (WASP) water transport model are used (Ambrose et al. 1995).

4.4.4 BIOTIC PROCESSES

The transport of chemicals to biota (*i.e.*, into biotic compartments) consists of diffusive and advective processes, though the latter term is rarely used by biologists. Chemicals diffuse into plant leaves from air; chemicals deposit onto plant leaves with particles in air, an advective process. The uptake of chemicals from soil or water in soil by plant roots or earthworms is treated as diffusion, though water carries the chemical into the plant (advection). Similarly, chemicals are assumed to enter algae, macrophytes, and benthic invertebrates by diffusion. The major advective process for animals is food intake by fish, birds, and mammals.

The only transport process within biota that is included in TRIM.FaTE is transport between roots and leaves through the plant stem in xylem and phloem fluids. The distribution of chemicals among organs in fish and wildlife is not a feature of TRIM.FaTE.

4.4.5 REACTION AND TRANSFORMATION

Reaction and transformation processes include biodegradation, photolysis, hydrolysis, oxidation/reduction, and biotic metabolism. These are processes that transform a chemical species into another chemical species. Reaction and transformation are modeled in TRIM.FaTE as reversible reactions using first-order reaction/transformation rates (or, equivalently, transformation half-lives). The first-order transformation rates may incorporate more than one of the processes involved. Depending on the algorithm and compartments involved, the mass of chemical transformed may be either lost from the system (*i.e.*, transferred to a sink), or tracked as a different chemical.

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